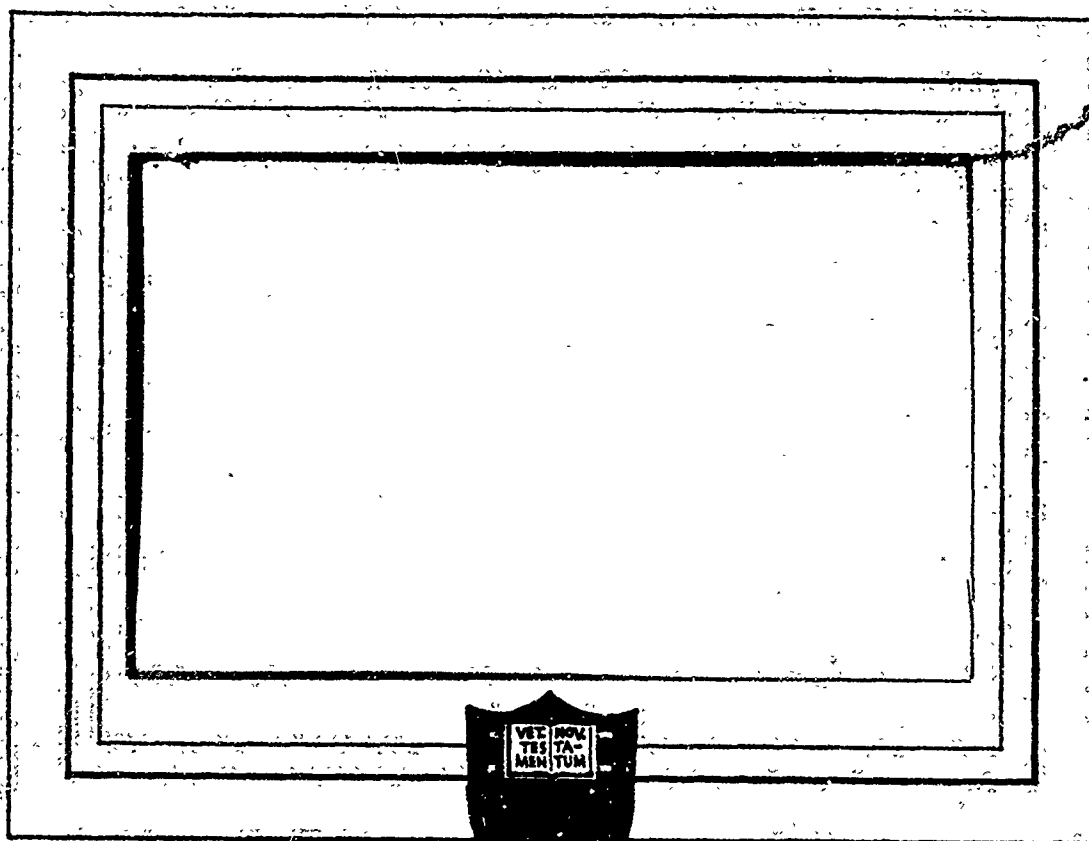
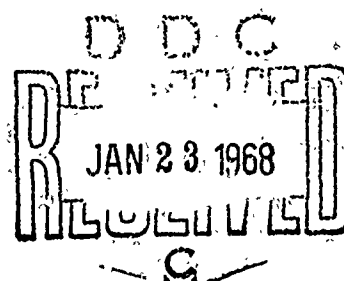


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RADIATION AUGMENTED BURNING OF A SOLID PROPELLANT

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by

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Transmitted by:


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ABSTRACT

The potential role of exothermic binder-oxidizer interactions at or below the burning surface in the steady-state combustion of composite propellants has been the subject of considerable debate in recent years. Such interactions have been considered to be insignificant by some investigators and by others to be the dominant factor in determining propellant burning rates. The work reported here comprises an attempt to determine in a unique manner the importance of such a heat release term in low pressure combustion.

The experimental conditions are designed to force extinction of the gaseous binder-oxidizer diffusion flame so as to study the gasification processes at or beneath the surface of the composite solid isolated from the normally adjacent flame; this requires extremely low pressures. Radiation from an arc image furnace is then directed at the surface to provide a substitute forcing function for this gasification. In this arrangement, the radiative flux replaces the usual conductive heat flux from the gas flame to the surface. A specific point of interest is the variation (if any) of regression rate with oxidizer particle size under these conditions; such a variation might be taken as an indication of binder-oxidizer interaction in the condensed phase, on the assumption that regression by a simple gasification process without bipropellant reaction would be independent of particle size. A second point of interest in the experiments is to measure quantitatively the radiation intensity in relation to the regression rate; this could be compared at each value of the regression rate with the feedback heat flux in normal steady-state burning calculated from a flame theory that includes no surface oxidation reactions. The difference, if any, would be a measure of the heat produced by such surface oxidation reactions.

The attainment of such a flameless regression condition has been definitely established in our tests only for one propellant composition; for other compositions the radiative input evidently shifts the flame extinction pressure to a level below the minimum attainable in the apparatus (5 mm Hg), i.e., the extinguished gas flame returns. With the return of the flame is an indeterminate amount of conductive heat flux to the surface, which complicates the experiment. Several undesirable side effects were found to exist due to the required experimental conditions. For example, approximately 50% of the ammonium perchlorate in the test samples was ejected from the regressing surface; strong indications were found aside from this ejection that the AP failed to behave in its usual exothermic monopropellant fashion but rather merely sublimed, probably endothermically. These and other complications which arose have precluded the possibility of achieving the original objective, i.e., of drawing any quantitative conclusions from this experiment with regard to the extent of exothermic binder-oxidizer interactions in the normally burning surface. On the affirmative side, the experiment brought out a number of physical and chemical details regarding low pressure inefficiency of burning that pertain to burning without radiative flux.

I. Introduction

The steady-state combustion of composite solid propellants is a subject of considerable complexity which has yielded only very slowly to the efforts of numerous researchers who have sought to elucidate its mechanism. The reasons for this become apparent when one considers the physical and chemical make-up of a typical composite propellant. A unimodal or multimodal distribution of oxidizer particles (most frequently ammonium perchlorate) is embedded in a continuous polymeric fuel matrix which gives the composite its structural integrity. The geometry of this composite is too complex to allow exact mathematical description and the flame structure which results from it is even more ill-defined. Diffusion processes patterned upon this complex geometry must evidently be important in the combustion since the oxidant and fuel species are initially unmixed.

The combustion chemistry is equally formidable. The reaction sequences whereby the polymeric binder and the oxidizer gasify are not well understood. Indeed, they are not necessarily independent; for example, binder gasification may be due as much or more to heterogeneous attack by oxidizer species than to purely thermal causes. The location and type of exothermic redox reactions that drive the combustion wave have not yet been firmly established. From a chemical point of view, it is not possible to rule out a priori solid phase, heterogeneous, or gas phase reactions. Obviously, the analysis of this intricate series of interrelated chemical and physical processes that comprises the combustion mechanism presents a considerable challenge.

It should be evident that a detailed mathematical theory for flame structure and flame velocity which takes into account all of the intricacies of the combustion process is beyond realization; fortunately, however, such a theory is not necessary. A simpler, yet physically sound theory which adequately accounts for the principal combustion processes would be a sufficient basis for the analysis of rocket motor behavior, both steady and unsteady.

There is still, however, considerable debate as to what constitute the principal combustion processes. For example, ammonium perchlorate is itself a monopropellant; the relative importance assigned to the monopropellant decomposition flame varies considerably with different theories. The debate also extends to other points; the one of particular importance here pertains to events below and at the propellant surface during steady-state combustion.

Present mathematical models of composite propellant combustion^{1,2} incorporate the assumption that the only chemical processes occurring at or below the propellant surface are the independent pyrolyses of binder and oxidizer. The former is generally taken to be endothermic; the latter (for the case of AP) is endothermic in its initial stages but exothermic overall due to the monopropellant character of AP. Since the AP comprises the major portion of the propellant, the overall gasification

process has a net exothermicity the magnitude of which is dictated strictly by the oxidizer to fuel ratio (according to the assumption of independent pyrolyses). Further heat release is assumed to result from a gaseous diffusion flame above the pyrolyzing surface which largely governs the propellant burning behavior. A question which has arisen with increasing frequency in recent years is whether these gasification reactions do indeed proceed independently. If the binder and oxidizer (or their decomposition products) can interact exothermically at or below the propellant surface to a significant extent this heat release could perhaps be sufficient to account for observed propellant burning rates (and thus be the key to explaining the burning behavior). In this view, which is essentially the opposite extreme from that described above, subsequent gas phase redox reactions merely constitute a sort of afterburning, which has little influence on the burning behavior.

The possibility of the existence of such solid phase or heterogeneous reactions has been suggested by several investigators^{3,4,5,6,7}. Purely solid phase redox reactions are conceivable in the region of intimate contact between binder and oxidizer around each oxidizer particle. However, since this contact would probably be destroyed by the very occurrence of such reactions, it seems likely that they could proceed only to a very limited extent and thus from the viewpoint of total energy release they would be of only minor importance. Heterogeneous redox reactions cannot be dismissed so readily, however. The decomposition of ammonium perchlorate liberates at various stages such gases as HClO_4 , O_2 , Cl_2 , NO_2 , and chlorine oxides. Anderson, et al.³, have suggested, but without evidence, that the attack of one or more of these gases on the fuel surface may constitute the chief exothermic reaction leading to composite propellant ignition. It is possible that such reactions could also proceed significantly at or below the surface during steady-state combustion. Pearson and Sutton⁴ recently presented what they considered to be evidence which tends to support the heterogeneous reaction hypothesis; they found that HClO_4 (and/or its decomposition products) ignites more readily with a fuel surface than with fuel vapor in the range of 200-300°C. Of course, the more meaningful comparison would be between a gas phase reaction at 2000-3000°C (fed by surface pyrolysis) and a surface reaction at 500-600°C; the Pearson-Sutton experiments are of no value in making this comparison. McAlevy and Hansel⁵ found that NO_2 and Cl_2 significantly enhanced the regression rates of polystyrene subjected to intense surface heating with a hot gas jet; a gaseous flame was reportedly absent (blown away, they believed) in these experiments and the authors thus concluded that these two gases react directly with the polymer in the condensed phase. Wenograd⁶ recently reported an increase in the low temperature exothermic decomposition energy of ammonium perchlorate in the presence of PBAA and polysulfide fuels and indicated that this may have been intimately related with the overall propellant gasification process. But the observed heat may have come from gaseous reactions as well as from heterogeneous reactions; the equipment offered no means for distinguishing the two. On the other hand, no evidence of exothermic surface reactions was found by either Hightower or West, et al.⁸ in propellant burning experiments, in which the extinguished surface region and the fuel-oxidizer contact region were examined photomicrographically to a resolution of a few microns. Obviously, the question is not yet settled to the satisfaction of both sides. The fuels used varied with the different experimenters and it is quite possible that the presence or

absence of heterogeneous reactions is strongly dependent on the type of fuel under investigation as well as the type of experiment and on the residence time in contact.

II. Experimental Objectives

The present work comprises a unique approach to this question of the possible existence of exothermic reactions within or at the surface of the condensed phase of a burning propellant. Note first of all that especially at low pressures where the thermal layer in the solid is thick, these reactions should have a strong dependence on the amount of interfacial area between binder and oxidizer. That is, the reactants can intermingle only in the "annular area" around each oxidizer particle. Thus the energy release per unit volume in the solid would vary inversely with oxidizer particle size if such reactions are possible. This variable energy release would yield a dependency of burning rate on particle size.

Now, it is well known that burning rate does indeed depend inversely on oxidizer particle size but this dependency is commonly assigned to diffusion effects in the gaseous propellant flame (and with good reason). Particle size effects in the gaseous flame should diminish at low pressures but one can never be assured that they have disappeared. Thus the search for particle size effects in the solid as indicators of sub-surface reaction is frustrated by the presence of the gas phase flame which may also exhibit such effects. The only way to circumvent this interference is to remove the flame.

Now, one cannot totally isolate the process of interest and hope to obtain meaningful results. The gaseous flame is a very important source of heat for the solid so that if it is removed, it must be replaced by a heat source of equal strength which shows no dependence on oxidizer particle size. Radiation would appear to fulfill this requirement quite well.

The desired experimental situation is then the following. A sample of a composite propellant is made to regress at a steady rate by means of externally supplied radiant energy. The gaseous flame that normally would consume the fuel and oxidizer pyrolysis products is prevented from forming by decreasing the pressure to such an extent that exothermic gas phase reactions are quenched by convective and radiative heat losses. The applied radiation is absorbed at the propellant surface and hopefully induces the same gasification processes at and below the solid surface as occur during normal combustion.

Now, if these gasification processes are purely endothermic, the surface regression is analogous to pure ablation; the regression rate is uniquely determined by the magnitude of the radiant flux. On the other hand, if the binder and oxidizer can interact exothermically below the solid surface (where the low ambient pressure is only weakly felt,) a second energy source is available to influence the regression rate. As mentioned previously, the magnitude of this sub-surface energy release would be particle size dependent; the smaller the oxidizer particle size, the larger the energy release rate per unit volume and the higher the sample regression rate at a given incident flux level. The primary objective is then to measure propellant regression rates as a function of particle size under these conditions; if regression rate does not vary with particle size under these conditions, there are no sub-surface redox reactions.

However, as will be seen later, the converse is not necessarily true. To anticipate the later discussion, the entire experiment is based on the proposition that there are only two ways in which particle size may affect the burning rate, either through the hypothetical solid phase reaction rate determined by contact area or through the gaseous reaction rate as affected by the scale of unmixedness, and it was hoped that no other particle size-dependent effects would intrude in the experiment. We knew of none. Unfortunately, other size-dependent effects did intrude, as we shall explain later.

III. Description of Apparatus and Experimental Technique

A. Arc Image Furnace

For the experiments as described in the previous section, one needs an intense, steady, and easily controlled source of radiant energy. These requirements are reasonably well satisfied by an arc image furnace¹⁰. Such a furnace consists of three main elements: the arc itself, an optical imaging system, and a suitable shutter. A schematic drawing of the arc furnace used in this work is shown in Fig. 1; an overall picture of the apparatus is shown in Fig. 2.

The radiation source is an electrical arc established between two carbon electrodes; the positive carbon is 9 mm in diameter and the negative carbon is 7 mm in diameter. The carbons are vaporized by the energy dissipated in the arc and thus must be automatically fed toward each other so as to maintain an approximately constant arc length. The front face of the positive carbon is positioned manually before each test by setting it in line with two 0.010" diameter fiducial wires mounted three inches apart on a line perpendicular to the optic axis. The arc is powered by a full wave rectifier; two high current chokes are placed in series with the arc so as to reduce the ripple in the output light intensity below 5%. The arc is normally operated at an input power level of 1500 watts (50 amp. at 30 volts). Both arc current and voltage are monitored during testing.

Spectral distribution data have not been obtained for this arc. The carbons are doped with various compounds so as to increase the light output in the visible and the spectrum is not expected to be that of a black body. The spectral data for high current carbon arcs that have been published indicate that the radiation peaks near 0.5μ and that most of the energy lies between 0.4 and 1.2μ .

A sketch of the modified double-elliptical mirror system used in this arc furnace is shown in Fig. 1. Radiation from the arc (primarily from the very hot crater region in the positive carbon) is collected by the first elliptical mirror; this mirror and the second elliptical mirror are positioned so that their secondary foci coincide. Thus the radiation, in being transferred to the second elliptical mirror, passes through this common focus; the reduced beam cross-section permits relatively easy shuttering. This is the reason for the use of two confocal elliptical mirrors. From the second elliptical mirror, the radiation passes to the spherical

mirror and then into the combustion chamber where it impinges on the surface of the propellant sample.

The spherical mirror has been added to the system for two reasons. First of all, it decreases the half-angle of beam convergence on to the sample from 75° to 45° . This gives an appreciable increase in the "depth-of-field" in the focal region, i.e., the variation of flux level along the optic axis is decreased appreciably. This makes sample positioning along this axis less critical. This advantage has been made somewhat superfluous, in the meantime, by the addition of a manual sample feeding device to be described later. By displacing the focus to a point external to the confines of the optical system, the spherical mirror removes all constraints on the size and shape of the combustion vessel. This is necessary to permit a vessel design in which the main window can be kept free from deposits of pyrolysis products; this point will be discussed further later. The use of the spherical mirror has one major disadvantage; it decreases the maximum attainable flux level considerably. The maximum radiant flux in the present system is $12 \text{ cal/cm}^2 \text{ sec}$ (over a .6 cm. dia. circle); however, this is adequate for the experiments described herein.

The function of the shutter is to provide an exposure of known duration and shape (flux vs. time). It consists essentially of two aluminum plates moved in opposite (vertical) directions by two double-acting pistons. The solenoid valves which supply gas to and bleed gas from the pistons are connected to a timer relay so that the total exposure time can either be pre-set or controlled manually by the operator. Opening and closing times of the shutter are approximately 30 msec.; since typical exposure times are of the order of ten seconds, the flux vs. time is essentially a square wave (assuming a constant arc output). When the shutter is half-open it trips a timer which measures exposure time with an accuracy better than one-tenth of a second.

B. Flux Calibration

The radiant flux level in the focal region of the arc image furnace is measured with a calorimeter similar to that described by Beyer, McCulley, and Evans¹¹. It consists of a small platinum disk whose front face is coated with platinum black; a chromel-alumel thermocouple, soldered to the back of the disk, senses its temperature. A 0.005" thick plate with a 0.27 cm dia. aperture is placed in front of the disk. The disk is designed to be large enough to capture the entire convergent-divergent beam entering the hole. Conduction in the disk is sufficiently fast so that it essentially responds as a unit, i.e., it serves effectively as an integrator of the flux passing through the aperture. Thus a constant flux yields a thermocouple EMF which increases linearly with time; the slope of the line is proportional to the flux. From this slope and the known properties of the disk, one calculates the average flux over the aperture area.

By mounting the calorimeter on a suitable adjustable stage, one can effectively obtain a three-dimensional map of the focal zone inside the combustion chamber. Typical data are shown in Fig. 3; the

percentage variation of flux with distance shown there is appreciably less than that found at the focus of the second elliptical mirror (the usual working point in double elliptical systems). The scatter in the data is indicative of the degree of non-reproducibility in the arc output for a fixed power input. This variation is presumably the result of random variations in the position of the crater in the positive carbon relative to the focal point of the first elliptical mirror.

C. Combustion Chamber and Gas Control System

The tests are conducted in an enclosed vessel so as to permit better control of the sample environment. A photograph of the combustion chamber used in these experiments is shown in Fig. 4. It consists of a 4 in. dia. stainless steel cylinder in one end of which is a 3 1/2 in. dia. window; the radiation passes through this window. The sample holder is inserted into the opposite end of the cylinder. Two 3/4 in. dia. windows on opposite sides of the cylinder provide a fiducial line of sight directly across the sample surface. The sample holder is provided with a manual screw feed so that by sighting through one of the side windows, one can (with a little practice) maintain the surface of the regressing sample flush with the face of the sample holder during a test. Thus the sample surface does not regress through the focal region but rather remains fixed. The hole in the face of the sample holder through which the sample "protrudes" is only a few thousandths of an inch larger than the sample diameter (approx. 1/4 in.) so that very little radiation is incident on the sides of the sample. Geometric factors that could lead to a variable or ill-defined incident radiant flux are thus eliminated.

As stated in Section II, flame formation is prevented by conducting the tests at very low pressures. The combustion chamber is evacuated by means of a vacuum pump with a pumping speed of 100 ft.³/min. (a 2" Dia., 100 ft. line connects the pump to the apparatus); the vacuum system is coupled to the combustion chamber via a 1 in. ID port in the top of the chamber. Pressure variations in the chamber due to the cyclic action of the pump or minor gas influx variations are effectively eliminated by a 10 ft.³ ballast tank just downstream of the chamber. Chamber pressure is measured with a mercury manometer in the range 10 to 150 mm Hg and with a McLeod gauge in the range 0-10mm Hg. The chamber pressure is controlled both by means of a valve in the vacuum line and by the use of a nitrogen flow which bypasses the chamber itself.

The problem of keeping the main window of the combustion chamber clean during a test was alluded to in Section III-A. This caused considerable difficulties in early tests. A powdery white substance (presumably sublimed ammonium perchlorate) deposited on the window as soon as sample regression commenced; it thereby caused a monotonic decrease in the radiant flux incident on the sample during the course of a test and thus invalidated the results. This problem was overcome by careful design of a purge system for the window. The glass is offset approximately 0.005 in. from the shoulder on which it normally rests by three small pieces of shim stock. A nitrogen flow is

introduced into the combustion chamber through this small gap around the rim of the window. This flow is funnelled toward the sample by a truncated cone (half-angle of convergence equal to 45° , i.e., same as beam convergence half-angle). The flow emerges from the cone approximately one inch from the sample surface. Its momentum is sufficient to overcome the momentum of the hot gases emerging from the sample surface so that they cannot impinge on the window. The resulting mixture of gases is continually withdrawn from the chamber through the vacuum system.

This nitrogen purge has two other effects. First, since it flows directly at the sample it forces flame extinction (via convective cooling) at a higher pressure than would be observed otherwise, but it is believed that the cooling is not so intense as to invalidate the presumed adiabatic relation between the radiative flux intensity and the measured regression rate. (See Section IV-B below.) Second, it imposes a limit on the minimum attainable pressure in the combustion chamber. The minimum nitrogen flow rate effective in keeping the window clean turned out to be 5000 cc/min (STP) in this design; the corresponding minimum chamber pressure was 5mm Hg. This purge rate was used for all tests.

D. Flame Detection System

The hypothesized experimental situation is one in which no flame exists. Obviously then it is necessary to establish that this is or is not the case for any given set of experimental conditions, and therefore some means for detecting the presence of a flame is needed. This is not the trivial problem that it might appear to be at first sight. The extreme brilliance of the radiation incident on the sample completely overrides the weak luminescence of a low pressure solid propellant flame, so that the latter cannot be detected visually. Furthermore, a simple thermal detector such as a thermocouple in the space above the regressing surface is of little use, since it is strongly heated by the radiation field.

A sensitive optical detection system has been developed and employed successfully in measuring the extinction pressure of a propellant flame during irradiation from the arc. It consists of a grating monochromator, photomultiplier, (1P28, peak sensitivity at 3400°A) and associated electronics. Ultraviolet radiation is removed from the arc light by a 2mm. thick piece of Jena glass GG-9 placed near the arc shutter; this glass has essentially no transmission below 4200°A . The monochromator views the space directly above the sample surface through one of the (quartz) side windows in the combustion chamber. Any flame radiation in the spectral band under investigation passes through the monochromator and into the photomultiplier; any scattered visible light that may pass through the monochromator is absorbed before it reaches the photomultiplier by a Corning 7-60 filter which transmits only below 4000°A . Since the flame radiation, when present, is extremely weak, it is necessary to amplify the photomultiplier output considerably. This is done with two DC amplifiers in series yielding the required amplification of 5000 to 10,000 times. The second amplifier is provided with a built-in variable low

pass filter normally operated at a 10 cps cutoff so as to eliminate circuit noise. The filtered output of the second amplifier is fed to a Visicorder oscillograph for recording. The magnitude of the Visicorder galvanometer deflection is measured as function of chamber pressure in order to detect flame extinction.

E. Test Procedure

Propellant samples are machined to the desired diameter (approx. 1/4") on a small lathe. These cylindrical pieces are then cut into 1/2" lengths with a clean, new razor blade. The surface to be exposed is always the result of such a cutting process. The side surface of the sample is not inhibited in any way since the sample holder design precludes burning on the side.

After the initial sample length has been carefully measured, the sample is placed in the holder and the latter inserted into the combustion chamber. The chamber is evacuated and then purged by the nitrogen flow entering around the rim of the main window (this flow is monitored by means of a rotameter). The desired chamber pressure level is set usually by adjusting the magnitude of an auxiliary nitrogen flow introduced downstream of the chamber. Meanwhile, the arc has been struck and allowed to equilibrate (for approx. 5 min). When these preparations are completed the arc gap is carefully set at 1/4" and the positive carbon precisely aligned with the sighting wires described previously (so as to reproduce the flux calibration conditions). Immediately thereafter the test is begun by opening the shutter (which starts the exposure timer). After a short ignition delay, the sample begins to regress, and from then on it is fed in manually so as to maintain the surface in a constant position. The exposure time of most tests is controlled by the operator so that a total regression of 1/8 to 1/4 in. is obtained. After the exposure, the final sample length is carefully measured and the exposure time noted (typical exposure times are 10-15sec.); the ratio of sample regression distance to exposure time (corrected for ignition delay) is the burning rate for the given conditions. Ignition delay was originally determined by extrapolating to zero regression the results of a series of tests with varied exposure times; it was later found that satisfactory results could be obtained by visual measurements using a stopwatch.

The methods of burning rate and ignition delay measurement and the reliance on a pre-determined flux calibration are all rather unsophisticated techniques and could, of course, be improved. However, the purpose of all of the tests described herein was to investigate the validity of the basic experimental approach; for this purpose, the methods used were adequate.

IV. Results and Discussion

As described in Section II, the central idea of the experiment is the measurement of propellant regression rate as a function of oxidizer particle size under flameless conditions in order to obtain evidence as to the possible existence of sub-surface exothermic reactions. The idea is both novel

and simple, but it is not obvious a priori whether it is capable of producing useful results. This last is, of course, true of any proposed experiment for which it is not possible to quantitatively predict the magnitude of undesirable side effects. As will be seen from the results to be described below, a variety of side effects that depend on particle size do arise in this experiment in such a way as to make its usefulness quite dubious.

A. Flame Extinction Pressure

The flame detection system was described in Section III-D. It was originally intended that the system be used to detect either the CN bandhead at 3883Å or the NH bandhead at 3360Å. However, the intensity of both of these was found to be too low to allow positive identification. Since the normal flame spectrum contains no other lines of sufficient intensity in the spectral region where the detection system is sensitive it was decided that some additive was necessary to produce such a line. The tables of relative line intensities of various elements in flames given by Dean¹² indicate that cadmium is best suited for this purpose; it has an intense single line at 3261Å which is thus very near the peak photomultiplier sensitivity (3400Å). Initial attempts to produce a PBAA/AP propellant with 1% of either anhydrous or hydrated cadmium chloride yielded samples that could not be fully cured (perhaps the electrophilic nature of these compounds causes them to act as chain breakers during polymerization). Satisfactory samples were subsequently prepared with 1% cadmium metal powder (98% through 325 mesh). Cadmium metal has a very low melting point (320°C) and boiling point (770°C at one atmosphere); it therefore should vaporize readily even if the propellant flame temperature is reduced by incomplete combustion. Qualitative spectra obtained with this propellant at 100mm Hg in a low pressure strand burner confirmed that cadmium does indeed yield a line of much higher intensity than those of either CN or NH.

The results of a series of tests on the composition 75% AP (80 micron), 23% PBAA, 1% carbon black, 1% cadmium metal are shown in Fig. 5; these indicate that flame extinction occurs at approximately 5mm Hg for this composition. The fact that the galvanometer deflection plotted in Fig. 5 does indeed represent the cadmium line intensity is confirmed by merely rotating the monochromator grating during a test; the deflection drops to zero on either side of the 3261Å line. The large spread in the point at 12mm Hg is quite interesting; the galvanometer deflection was observed to vary sharply from zero to a relatively high value several times during the test. This suggests that at this pressure, the flame is marginally stable so that it flickers on and off; when the pressure is dropped to 5mm Hg the flame cannot form at all. The initial increase in galvanometer deflection with decreasing pressure is quite surprising. One would expect that if the flame is getting weaker (i.e., cooler) as the pressure is decreased, the line intensity (and therefore the galvanometer deflection) would also decrease monotonically. The observed behavior is possibly due to effect of pressure on oxidation of the cadmium; oxidation is certainly to be expected in such an environment. Decreasing pressure favors the oxide dissociation reaction so that a greater

concentration of the free metal is available to contribute to the line intensity; however, flame extinction ultimately forces the line intensity to zero.

Note in Fig. 5 that the normal extinction pressure for this composition, as determined in the low pressure strand burner, is approximately 40mm Hg. The reduction in the extinction pressure by the incident radiation is not surprising. The probable cause of normal extinction is a radiative heat loss from the propellant surface (rather than from the gas which has a much lower emissivity) coupled with a slowing of the gas flame reaction by cold gas dilution. In this experiment the externally supplied radiation overrides this heat loss so that only the gaseous flame itself is extinguished. This occurs at some lower pressure at which convective and radiative heat loss rates overpower the heat production rate of the gaseous flame, e.g., at 5mm Hg for the composition tested.

Now, the composition tested is fairly representative of all other formulations used in this research program. The presence of the cadmium is unique, of course. However, unless it is a catalyst, the small quantity added should have no significant effect on the propellant extinction behavior. The heat of vaporization of cadmium, 200 cal/g, is of the same order as the heat of pyrolysis of a typical binder. The measured normal (no incident radiation) extinction pressure 40mm Hg, is quite typical of other PBAA/AP propellant strands tested. Thus it appears likely that all similar formulations will exhibit a flame extinction pressure (with incident radiation) of magnitude comparable to that reported above.

This is detrimental to the experimental objectives for three reasons. First, as was mentioned previously (Section III-C) the lower pressure limit of the apparatus is 5mm Hg; thus there is virtually no latitude in which to examine possible pressure effects under the desired flameless regression condition. Second, the useful range of oxidizer particle sizes is probably restricted. The normal extinction pressure generally decreases with decreasing particle size; this is probably also true of the gas flame extinction pressure, so that flameless conditions would be unattainable in the present apparatus below some average particle size. Finally, there is the fact that such a low gas flame extinction pressure restricts the tests to a region that is very far removed from pressures of practical interest. As will be discussed later, there is reason to believe that the processes occurring in this region are not representative of the normal combustion processes.

B. Burning Rate Results

Prior to the completion of the flame detection system, a series of burning rate measurements was made with incident radiation in order to obtain preliminary data on the effect of oxidizer particle size and to determine whether gas flame extinction would exhibit itself by means of a significant change in the qualitative behavior of the results. Specifically, one would expect a rather sudden decrease in slope (perhaps to zero) of a plot of burning rate vs.

pressure in the neighborhood of the gas flame extinction pressure; this follows from the fact that the remaining gasification process should be either pure solid-to-gas pyrolysis with only a weak dependence of pyrolysis heat (plus or minus) on the pressure, or a pyrolysis augmented by sub-surface reactions which are largely insulated from environmental pressure effects.

The results of these tests are shown in Fig. 6; the compositions used all consisted of 75% AP, 24% PBAA, and 1% carbon black; oxidizer particle size was varied by a factor of twenty. Carbon black serves both to decrease the reflectivity of the samples and to increase their in-depth absorptivity (i.e., decrease the radiation penetration depth, at least in the binder). It is evident from these results that there is indeed a decrease in slope as the pressure decreases. The decrease is most pronounced for the propellant containing 300 μ AP; the slope drops to near zero at about 15mm Hg.

Unfortunately, it is not possible to draw a firm conclusion from this overall behavior because there is at least one alternative basis on which it can be explained. As the pressure is decreased, the heat feedback (per unit mass) from the flame either remains constant or decreases (as the flame weakens); however, the radiative heat input from the arc (per unit mass) increases because the burning rate decreases. Thus the pressure-independent radiative heat input will cause a gradual flattening of the burning rate curve. This flattening would occur, as the pressure is reduced, when the radiative input becomes comparable to the normal flame heat feedback; the regression rate would remain constant below this leveling-out pressure, all the way down to the lowest pressure attainable in the chamber. The curves of Fig. 6 seem to bear this out.

There is no adequate way in which to measure or calculate this heat feedback from the gas flame. However, one can attempt a simple surface heat balance based on the assumption that the flame is not present to see if consistent results are obtained. Equating the absorbed radiant energy to that required for steady-state endothermic pyrolysis, one obtains

$$(1 - r)I_o = \dot{m} [Q_p + Q_T + C_s(T_s - T_o)]$$

where

r = reflectivity of sample

I_o = incident radiant flux, cal/cm²sec

\dot{m} = mass burning rate, g/cm²sec

Q_p = effective heat of pyrolysis, cal/g

C_s = heat capacity of solid, cal/g^oC

T_s = surface temperature, ^oC

T_0 = initial temperature of solid, °C

Q_T = endothermic heat of AP crystal phase transition, cal/g

The question is whether the above equation can be satisfied by the experimental values for I_0 and \dot{m} in the pressure region below the break in slope. If so, this would indicate that the sample regression in this region is indeed a purely endothermic pyrolysis; if some additional energy input term is required to satisfy the equation, the energy source may be either the flame, exothermic sub-surface reactions or, within limits, the AP decomposition flame. The latter three possibilities cannot be distinguished on this basis.

A further factor enters in here which severely hinders the use of the above equation; this is the phenomenon of ammonium perchlorate particle ejection. Some large, but not precisely known, fraction of the AP is ejected from the surface without being fully gasified; the best present estimate is that about 50% of the AP is ejected in this way (this will be discussed further below). Obviously this alters the effective value of the heat of pyrolysis at the surface.

Using this percentage and also: heat of dissociation of AP¹³:
 $\text{NH}_4\text{ClO}_4(\text{s}) + 500 \text{ cal/g} \rightarrow \text{NH}_3(\text{g}) + \text{HClO}_4(\text{g})$; pyrolysis heat of PBAA:
 $\text{PBAA} + 150 \text{ cal/g (est.)} \rightarrow \text{low molecular weight hydrocarbon molecules}$;
 $Q_T = 20 \text{ cal/g}$; $T_s = 450^\circ\text{C}$ (50°C lower than that measured by Powling and Smith¹⁵ for a 5% AP/25% rubber propellant sample at 1 atm.);
 $I_0(1-r) = 8 \text{ cal/cm}^2\text{sec}$; $C_s = 0.3 \text{ cal/g}$. For the 300 μ AP samples at 5mm Hg the two sides of the heat balance equation differ by only 20%; this is close enough to indicate that both the AP and O/F flames are extinguished for this case (especially considering the imprecision of the AP ejection rate) and the regression is essentially an endothermic pyrolysis.

Since the 45 μ AP and 15 μ AP samples exhibit higher regression rates for the same radiative input, they obviously will not satisfy the equation unless an increased AP ejection rate is entirely responsible for the regression rate increase. However, for the 15 μ AP samples this would require that approximately 90% of the AP be ejected; this seems extremely improbable in view of the suspected ejection mechanism (to be discussed below). The observed particle size effect is consistent, however, with the persistence of a gas flame of some kind, either the monopropellant AP flame or the AP-fuel flame, down to 5mm Hg for the 45 μ AP and 15 μ AP samples, the effect being due to the influence of particle size on flame length (and hence heat feedback to the surface) and/or combustion efficiency. The decrease in slope would then be due to the fact that at these low pressures the radiative input is comparable to the heat feedback as explained above. This conclusion is also consistent with the discussion of the effects of AP particle size on extinction limit in the previous section. Note, however, that sub-surface reactions could also contribute to the particle size effect, although their existence seems less probable in view of the apparently endothermic behavior of the 300 μ AP samples at the lowest pressures.

Steinz and Summerfield¹⁶ have recently made a detailed study of the low pressure combustion and extinction behavior of composite propellants. In attempting to extend the granular diffusion flame theory¹ to this pressure regime, they found it necessary to include the behavior of the AP decomposition flame explicitly in the modified theory. Figure 7 taken from Ref. 16 effectively summarizes the results of their arguments. At high pressures (above 10-20 atm), the figure shows that the time constant characterizing the fuel-oxidizer flame is expected to be much larger than that of the AP decomposition flame; on this basis the authors show that this monopropellant flame has no significant effect on the kinetics of propellant burning rate. However, below 10 atm and especially below 1 atm the two time constants become of comparable magnitude and the detailed kinetics of the AP flame become quite important in determining the overall propellant behavior. Then, if the AP flame remains of second order and fully efficient (or at least as efficient as at high pressure) one would expect a burning rate vs. pressure curve that asymptotically approaches a slope of one as pressure approaches zero. However, various non-idealities enter the picture, as shown by the present work and that of Steinz. Of particular importance are combustion inefficiency and radiative heat loss from the propellant surface; the former is probably more significant than the latter in causing extinction in most propellants at pressures of the order of one-tenth of an atmosphere. The exact cause of this inefficiency, particularly with regard to the AP flame is not known at present. One can speculate, however, that the AP flame is strongly dependent for its very existence on the presence of the subsequent oxidizer-fuel flame (the former extinguishes at approximately 26 atm in the absence of additional fuel or catalysts). Thus as the oxidizer-fuel flame becomes greatly distended at low pressures and consequently subjected to significant convective dilution and cooling in the usual experimental set-up, its sustaining effect on the AP flame becomes less and less effective; finally, since the two are mutually inter-dependent, they are quenched simultaneously. Experimental data in Ref. 16 suggest that as this limit is approached the efficiency of overall combustion (for example, in terms of percent of available heat that is actually released) drops rather slowly with decreasing pressure and then suddenly falls to zero at the limit.

C. Ammonium Perchlorate Ejection

The substitution of radiation for the conductive flame heat feedback is obviously not a perfect one. First of all, the propellant has some finite overall reflectivity; some portion of the incident radiation merely bounces off the surface and serves no useful purpose. However, this reflected fraction probably amounts to less than 20% and, in any case, is a relatively simple factor to account for. Second, the propellant has some effective overall attenuation, that is not infinite, and therefore the non-reflected radiation is absorbed in depth. Some measured values of propellant attenuation are shown in Fig. 8; these were obtained with an infrared radiometer using the arc as the light source. The variation of attenuation with thickness is due to the fact that the light source is polychromatic. However, one sees from these results that very little radiation penetrates deeper than about 100-200 microns below the surface. This in-depth penetration would cause some distortion of the temperature profile in the solid, but its effect on the regression rate would probably not be significant. The heat balance equation in Section IV-B would not change.

Examination of the effects of reflection and in-depth absorption from such a macroscopic viewpoint is too simple, however. One must look more closely at the fact of radiation incident separately on exposed fuel and exposed oxidizer. The fraction reflected by each is a function of the refractive index of the material; the indices of typical binders and of AP are probably of the same order so that their reflectivities are not drastically different. However, some difference in heat input rate will exist due to this cause. It is in-depth absorption which compounds this difference. The binder in these tests is rendered opaque by the addition of carbon black (for the specific purpose of increasing the gross absorptivity of the samples); therefore energy deposition in it occurs very near to the exposed surface. However, there is no obvious way in which AP can be similarly opacified, and hence it remains transparent to radiation in the visible and near infrared region (up to approx. 2 microns). It is this transparency of the AP which is the probable (though not the only possible) cause of AP ejection.

The phenomenon of AP ejection first became evident in tests with relatively large (greater than 100 microns) AP particle size distributions. During such tests, the particles can be seen carried along with the emitted gas stream, as they pass through the luminous field adjacent to the sample surface; the particle streaks can be seen in Fig. 8. Photographs provide the only measurement yet obtained of AP ejection, but AP particle accumulation in the chamber also confirms its existence.

Ejected AP mass efflux rates are obtained in rough numbers from these photos by counting the number of particle tracks originating at the sample surface during the exposure time (which is determined by the camera shutter) and assuming the average particle size is unmodified. Obviously this ejection is a random process, and a single picture will not necessarily give the average ejection rate. For greatest accuracy, the exposure time should be as long as possible; the limitation in this direction is the fact the number of tracks becomes too numerous to allow clean identification of each (in particular whether a given track originates at the surface and hence during the shutter open time). Thus the appropriate shutter time is a function of the ejection rate; in Fig. 9, the exposure was 1/50 sec. As stated previously, this method indicates that the amount of AP ejection is of the order of 50% of the AP in the sample.

It was the intense radiation field which made this ejection evident; the logical question to then ask is whether this same ejection goes on undetected in normal low pressure combustion. Some preliminary tests have been conducted on PBAA/AP compositions, with and without copper chromite, in the low pressure strand burner (without radiation). Ejection was indeed found to occur in normal combustion, but the amount was greatly influenced by the presence or absence of the copper chromite. The propellant without copper chromite ejected on the order of 5% of the AP; samples containing 1% copper chromite ejected on the order of 50% of the AP. The technique used to obtain these results was again photographic (single pictures), hence these numbers are only rough estimates.

As indicated above, in the arc furnace tests, radiation may force the ejection of AP. The radiation can pass through AP crystals exposed on the sample surface and be somewhat focussed by them; it

would then be absorbed by the binder at the rear of the crystals causing vaporization of the binder and/or the AP. If the bond between the AP and binder remains intact around other portions of the crystal, there will be a pressure build-up behind the crystal which subsequently causes it to be ejected. Now, for PBAA there is noticeable charring of the binder at the sample surface; if this char depth is greater than or equal to the particle diameter, the pressure build-up behind a crystal would probably be precluded by the porous nature of the surrounding medium. Hence, one would expect on this basis that the AP ejection rate decreases with decreasing particle size. However, there is as yet no experimental data available to confirm this conclusion. In normal low pressure combustion, the copper chromite (which is a strong AP decomposition catalyst) may function in a similar way, i.e., it may cause localized vapor pockets at the immediate site of copper chromite particles which ultimately force the AP crystal to be ejected. One would expect a similar particle size dependence here, as well. Further study of this phenomenon is necessary before any definite conclusions can be drawn.

D. Combustion Inefficiency

The role played by the AP decomposition flame in steady-state combustion is not as yet clear. It is generally accepted, however, that this flame occurs much closer to the surface than does the binder-oxidizer diffusion flame. Since this is probably the case, there is some justification for assigning it to the general category of processes occurring at the propellant surface. Thus in devising the experimental conditions so as to give flameless regression (i.e., no diffusion flame), one hopes that this AP flame will not be greatly affected; its absence would mean the loss of an important exothermic forcing function for events at the surface.

However, there is strong evidence that under the experimental conditions employed in all the tests reported here, the AP flame is considerably retarded or perhaps totally absent. Extensive deposits of a white powdery material were always found to coat the inside of the combustion chamber during a test (this is what forced the use of the main window purge discussed previously). The material presumably was predominately AP; qualitative chemical analysis confirmed the presence of NH_4^+ and ClO_4^- ions, and it is difficult to envision what other white powdery substance could result from the propellant regression. The material is, then, probably the result of AP particle sublimation, i.e., some rather large fraction of the AP is not consumed by its own decomposition flame under the experimental conditions. This sublimation without combustion, perhaps endothermic dissociative sublimation, coupled with the considerable amount of AP ejection, constitute two very serious deficiencies in the experiment; as indicated, it was hoped that it would be possible to retain the normal surface gasification processes in the absence of the gaseous fuel-oxidizer diffusion flame (i.e., the AP monopropellant flame and the endothermic binder pyrolysis) so that these processes could be isolated and studied. However, the two phenomena of AP sublimation and AP ejection indicate that the combination of a radiative input and low environmental pressure strongly alter events at the propellant surface.

V. Future Studies of Ammonium Perchlorate Ejection

The ejection of ammonium perchlorate during normal, steady-state combustion warrants further investigation. Obviously, if it is an ubiquitous phenomenon, perhaps existing for some compositions even at normal rocket combustion pressures, it will necessitate considerable revision of present theories of steady-state combustion of composite solid propellants; therefore experiments will be carried out in the future in an attempt to characterize this ejection.

Although the real region of interest is the pressure range well above atmospheric pressure, experimental measurement problems necessitate that at least the initial work on particle ejection be carried out at sub-atmospheric pressures; here the flame is optically thin and of large dimension, thus permitting more detailed investigation. Of particular interest is the effect of binder-type and AP-decomposition catalysts on ejection rate. Surfactants to strengthen the surface adhesion of AP and binder should be tried. Another very important point is the variation of ejection rate with pressure; if the previously proposed mechanism of ejection is the correct one, the ejection rate would decrease with increasing pressure for several reasons. First, the thermal wave thickness decreases thus lowering the temperature around the submerged portion of an AP particle on the burning surface. Second, the time of passage through the thermal wave is decreased thus allowing less time for pressure build-up in a submerged vapor pocket. Finally, the vapor pocket pressure required to force ejection goes up with increasing external pressure. Thus it may be found that AP ejection becomes fortunately insignificant even at atmospheric pressure.

VI. Conclusions

This experiment was devised as a means of isolating the binder and oxidizer gasification processes peculiar to the surface and sub-surface regions of a composite propellant during low pressure combustion so as to allow a detailed study of their energetics. It was hoped that in this way it would be possible to determine the extent to which exothermic binder-oxidizer reactions in these regions contribute (if at all) to the overall burning behavior of a propellant. The desired condition of flameless regression with simultaneous radiative input was definitely achieved for one propellant composition only (that containing the cadmium additive); energy balance considerations indicate that it probably was also achieved for the 300 μ AP/PBAA composition tested. However, the appearance of the phenomena of AP ejection and combustion inefficiency indicate that the physical processes and energetics at the propellant surface are altered appreciably by the required experimental conditions. These factors coupled with the extremely low pressures necessary to prevent flame formation make it doubtful that data obtained from this experiment on the energetics of propellant gasification are applicable to normal combustion at pressures above one atmosphere.

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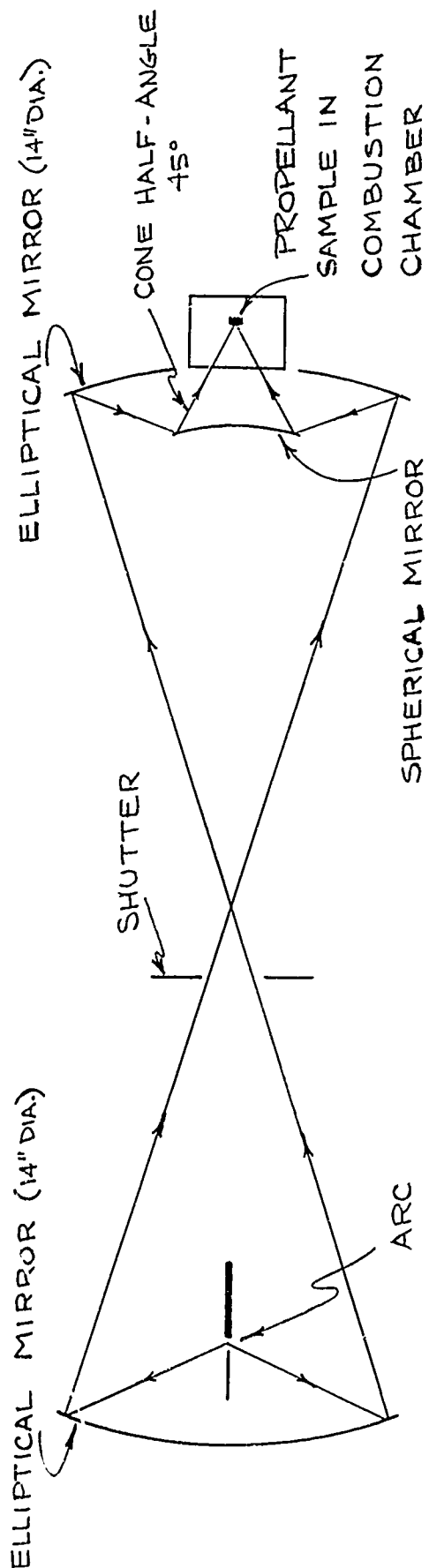


FIG.1 ARC IMAGING OPTICAL SYSTEM FOR RADIATION AUGMENTED BURNING EXPERIMENT

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Fig. 2 Overall view of radiative burning apparatus.

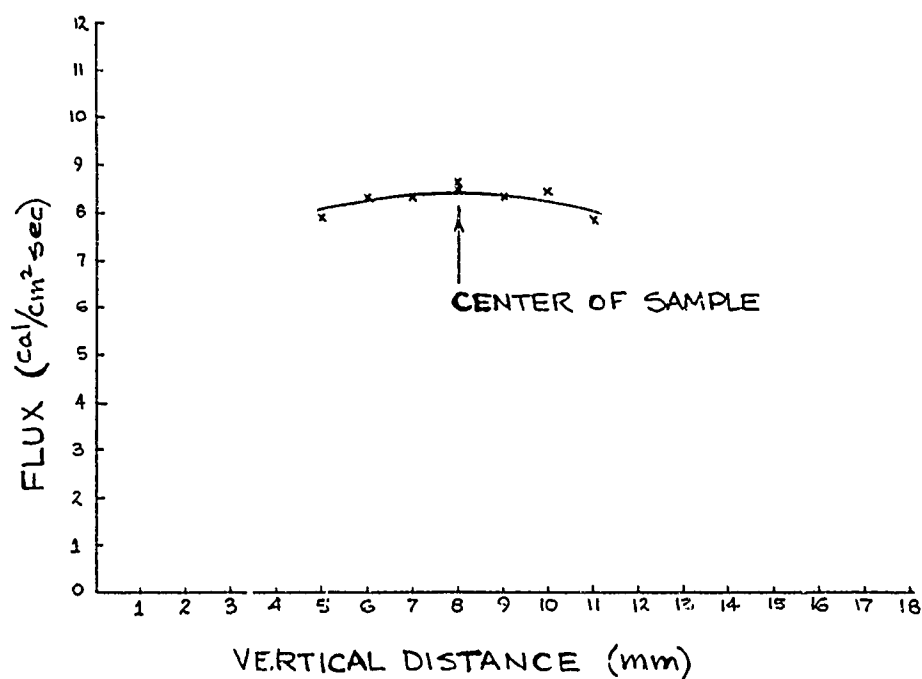
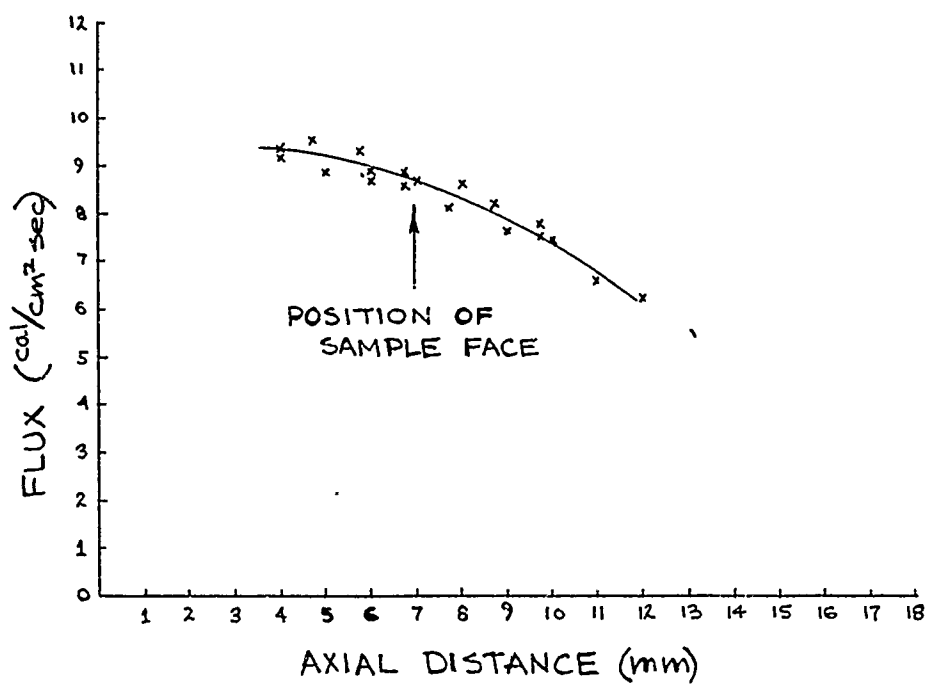


FIG. 3 FLUX MAP OF SAMPLE REGION

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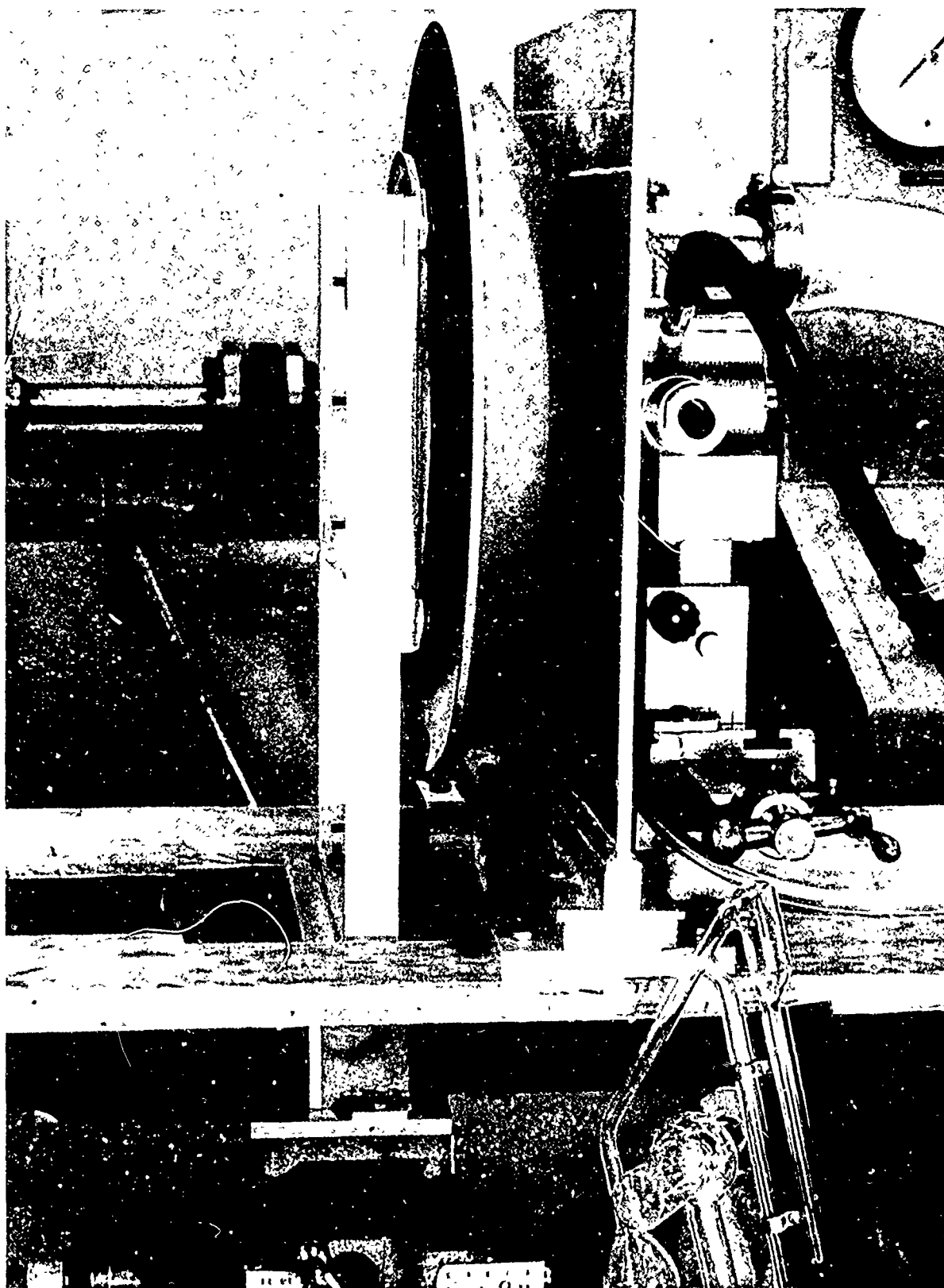


Fig. 4 Combustion chamber and collecting mirrors for imaging arc on sample; radiation enters from the left.

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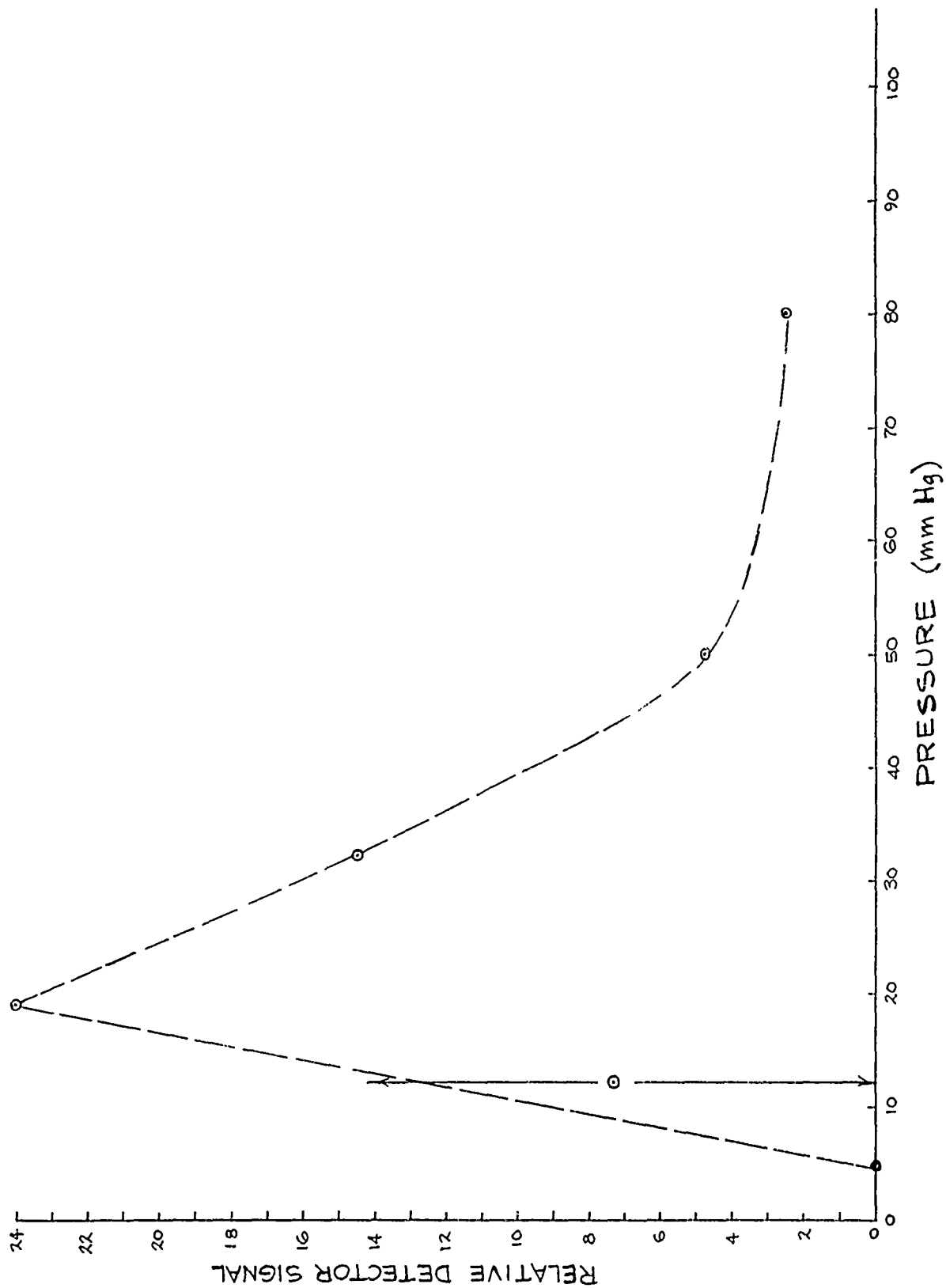


FIG. 5 RELATIVE INTENSITY OF 3261 Å LINE OF CADMIUM ADDITIVE

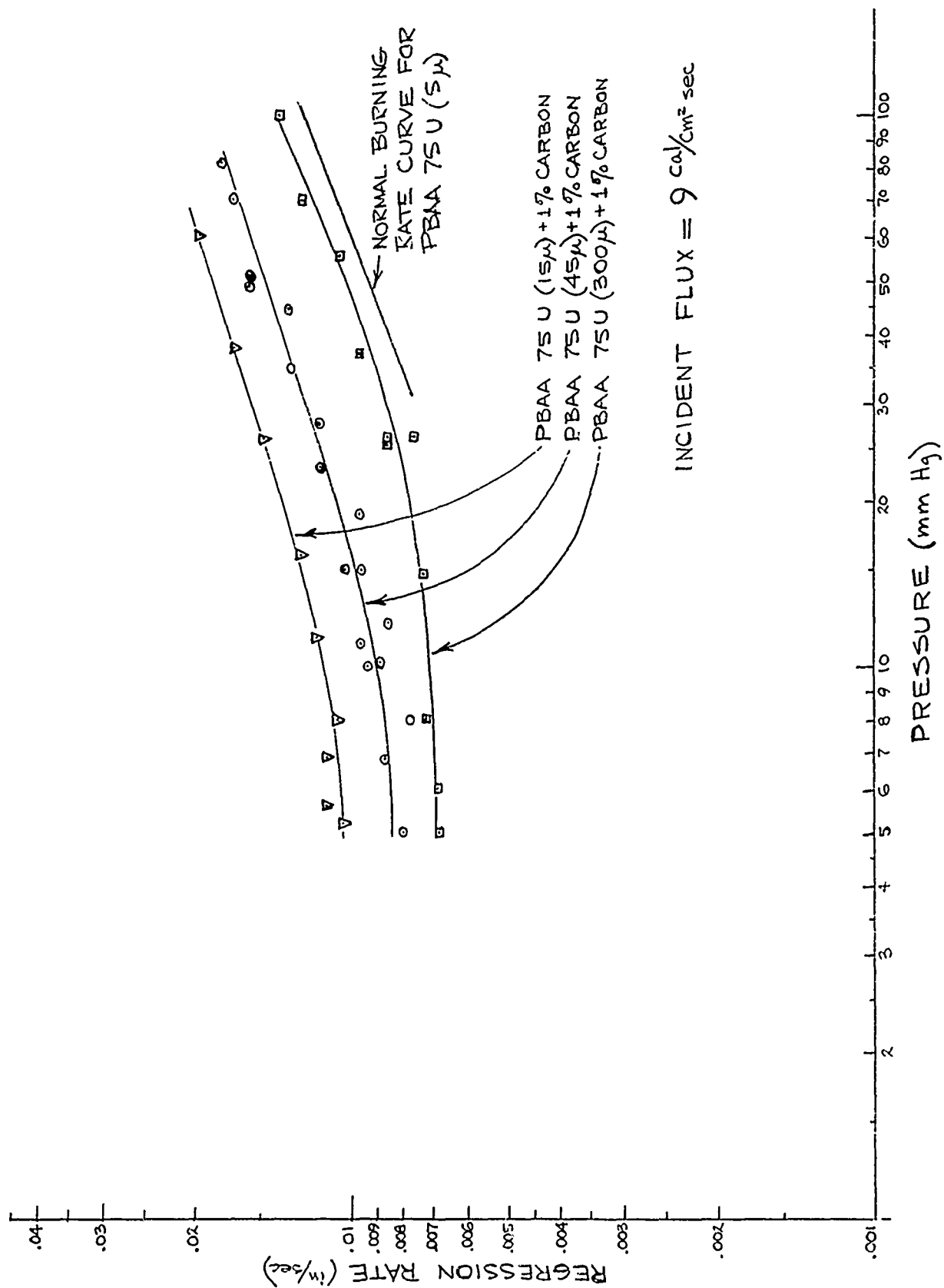


FIG. 6 INFLUENCE OF AP PARTICLE SIZE ON RADIATION-DRIVEN REGRESSION RATE

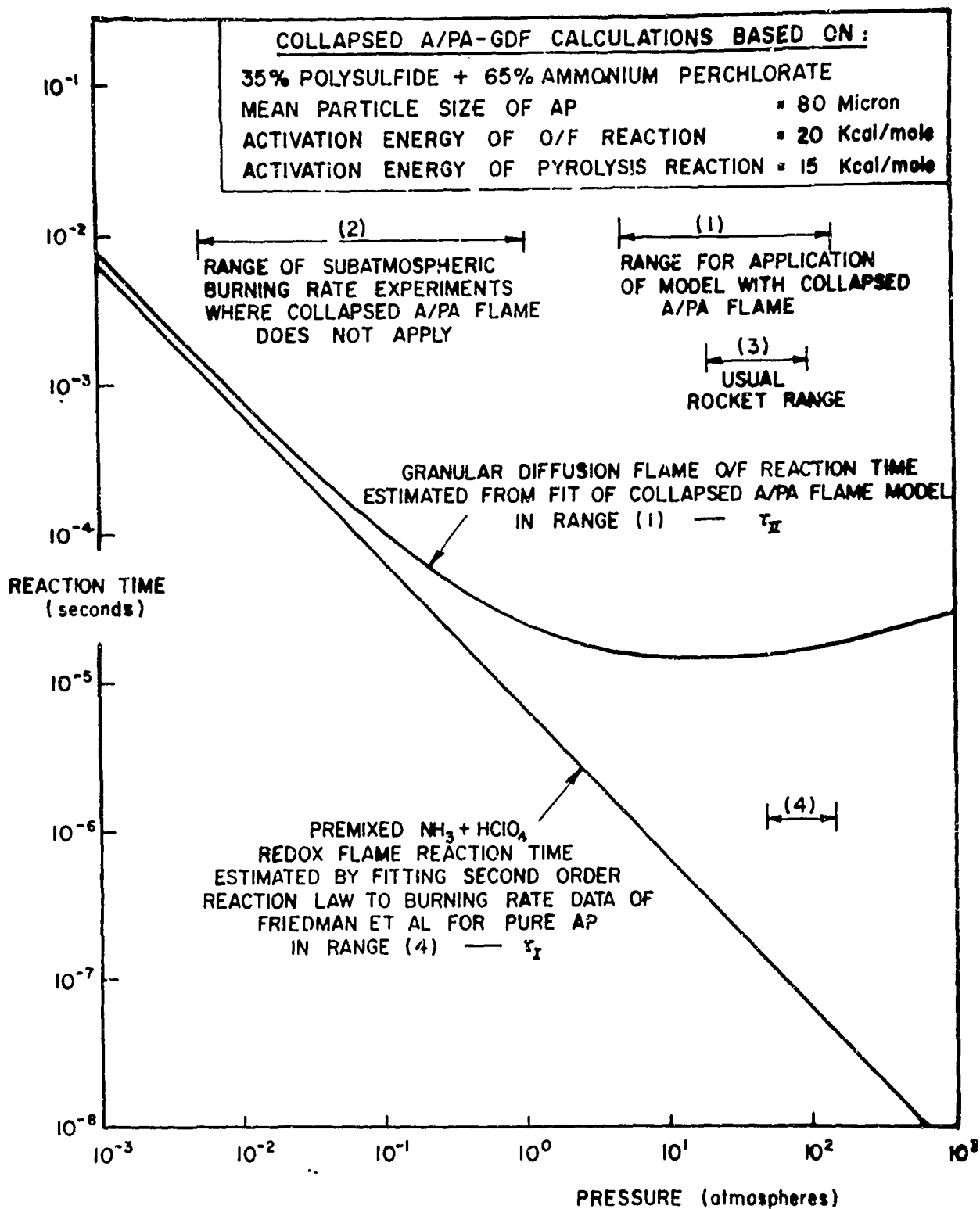


FIG. 7 PRESSURE DEPENDENCE OF REACTION TIMES OF AMMONIA/PERCHLORIC ACID AND OXIDANT/FUEL REACTIONS

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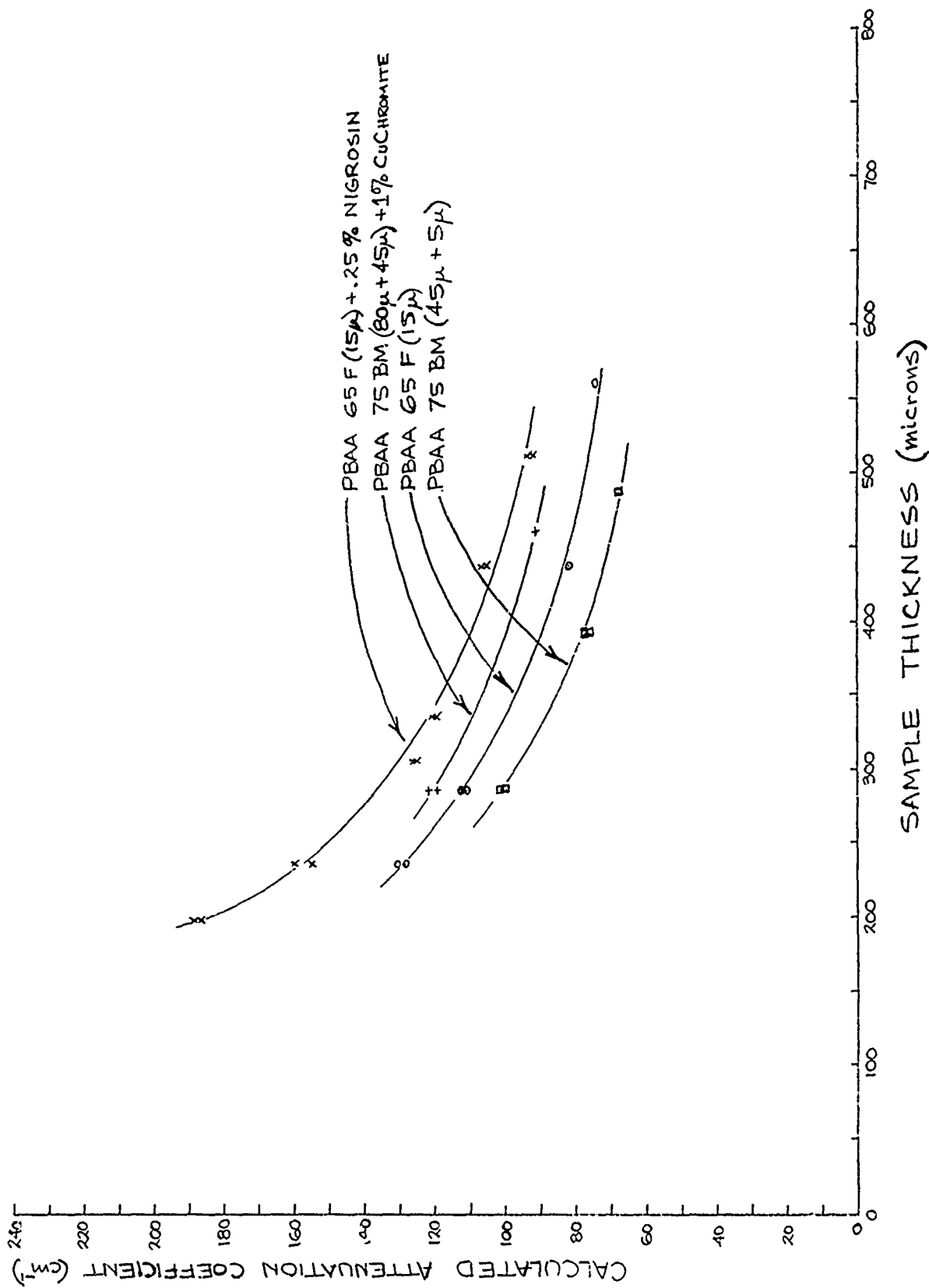


FIG. 8 TYPICAL PROPELLANT ABSORPTIVITIES FOR ARC RADIATION

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Fig. 9 Side view of AP crystals being ejected from propellant sample during irradiation; the crystal tracks are made visible by the arc light. Diffuse, crescent-shaped glow is reflection from window.

APPENDIX: DISCUSSION OF SOME ALTERNATIVE RADIATION EXPERIMENTS

The following material is based on an internal memorandum issued September 25, 1964, and comprises the results of preliminary studies of three possible experiments employing external radiation in the investigation of steady-state burning of composite propellants. Some of the comments have been updated.

A. Radiation addition to a burning propellant as a test of the granular diffusion flame theory.

If one makes the simplifying assumptions that none of the added radiation is absorbed by the propellant flame and that the transmissivity of the propellant is zero, the additional radiation term can be quite readily inserted into the granular diffusion theory.⁽¹⁾ Thus, the initial energy balance becomes,

$$\dot{m}C_s (T_s - T_o) - \lambda_g \left(\frac{dT}{dx} \right)_g - \dot{m}Q_s - \alpha I_{ex} = 0$$

where α = absorptivity of the propellant surface

I_{ex} = radiant flux incident on the surface

and the remaining terms retain their usual significance. This added term is carried throughout the normal derivation; it imposes no changes in the basic concepts. The final result has the form

$$\frac{1}{r} = \frac{C_1}{p^2} \left\{ a \pm (a^2 + C_2 p^2)^{1/2} \right\} + \frac{C_3}{p^{2/3}} \left\{ a \pm (a^2 + C_4 p^{2/3})^{1/2} \right\}$$

where C_1, C_2, C_3, C_4 represent groups of constants containing various propellant properties a is a constant times the absorbed radiant flux.

Note that if a is zero (i.e., no radiation is added) the equation reduces immediately to the usual form of the granular diffusion theory. The added algebraic complexity of the above formulation is quite evident, it does not appear possible to eliminate a priori either the + or - sign in the brackets. The equation can, of course, be recast in straight line form for a more critical comparison with experimental data; for example:

$$\frac{p^2}{r \left\{ a \pm (a^2 + C_2 p^2)^{1/2} \right\}} = C_1 + C_3 p^{4/3} \left\{ \frac{a \pm (a^2 + C_4 p^{2/3})^{1/2}}{a \pm (a^2 + C_2 p^2)^{1/2}} \right\}$$

The existence of the several constants comprising only approximately known and completely unknown quantities makes any practical usage of this equation quite difficult. (See note on page A-3)

Experiments of interest in an attempted verification of the above equation comprise those in which burning rate is measured as a function of incident radiant flux at constant pressure and those in which burning rate is measured as a function of pressure at constant radiant flux. Such a set of experiments imposes some difficult requirements on the apparatus to be used. For example, the burning propellant will quickly recede from the focal region of the arc furnace, especially at elevated pressures and/or high incident radiant fluxes. A manual

feed system for the propellant strands would very probably be inadequate so the only alternative would be the development of a fairly sophisticated servo system for automatic strand feed-in. Difficulties of an experimental nature such as this coupled with the questionable basis for interpreting results make this an unpromising avenue for research.

- B. Radiation input to a propellant under vacuum conditions designed to eliminate heat feedback to the solid surface.

Such research is designed to elucidate the nature of surface and/or subsurface reactions occurring during steady state combustion. The subatmospheric pressure and the external radiant flux should effectively eliminate the dependence of regression rate on heat feedback from any existing flame. There is a large degree of flexibility in formulating a theoretical model to be compared with the experimental data. Thus, one may postulate that reaction occurs only at the solid-gas interface or that it occurs in depth within the solid; one may postulate that the incident radiation is absorbed entirely at the surface or is absorbed in depth. The most important aspect of any proposed model is its specification of the dependence of reaction rate on pressure and oxidizer particle size. An attempt is currently underway to develop one or more theories embodying these considerations.

Experiments designed to verify a theory based on the above considerations would be analogous to those described under (A) above, i.e., the variation of burning rate with both radiant flux and pressure would be measured. Since a complete theory would attempt to predict the effects of oxidizer particle size, this parameter would also be varied. The apparatus necessary to carry out such an experimental program is not subject to the stringent requirements mentioned in (A) above. It is the results of this line of research which are discussed in the present report.

- C. Radiation input at one atmosphere and above with a gas jet designed to prevent a flame.

This line of research comprises a different experimental approach to the same questions concerning reactions in the solid mentioned in (B) above. The higher pressure brings the experimental conditions closer to those found in practical rocketry. The same theoretical considerations regarding spatial extent of reaction and radiation absorption apply; so also do the experimental considerations regarding burning rate measurement. A suitable model must also account for the convective heat loss to the nitrogen stream inherent in this approach. It is evident that the flow situation in such an experiment is very complex and is influenced considerably by such factors as roughness of the regressing sample surface and magnitude of the sample regression rate. The heat loss to the gas lowers the propellant surface temperature and thus in this sense the use of a gas jet to prevent a flame and allow study of the solid gasification is somewhat self-defeating; i.e., the decreased surface temperature suppresses the pyrolysis of the solid so that the processes one wishes to study are disturbed an unknown amount by the technique used. Despite these disadvantages, some preliminary experimentation based on this idea was carried out. The results showed a monotonic decrease of sample regression rate with increasing mass flow of the cross-wise gas flow rate; at very high flow rates, the regression rate tended asymptotically to a finite fixed value. However, the flow velocities required to yield this asymptotic value were of the order of 1000 ft/sec

and there was considerable evidence that this value was due largely to erosive effects of the gas stream rather than any fundamental propellant combustion process. Because of this fact and the other considerations mentioned above, the use of this technique for gaseous flame suppression was discontinued.

It was concluded, as a result of these preliminary studies of three ways of using radiation input as a test of the theoretical burning rate model, that the only method worth trying was B. This project was indeed carried out, and the results comprise the body of the present report.

NOTE REGARDING SECTION (A): Also under consideration was work designed to test the following equation from Ref. 17.

$$\frac{\Delta r}{r_o} = \frac{\frac{1}{2} \left[I_F + (1 - \alpha_F) \alpha I_{ex} \right]}{r_o \rho_p \left[C_s (T_s - T_o) - Q_s \right]} + \frac{\frac{1}{2} \left[\alpha I_{ex} - I_L \right]}{r_o \rho_p \left[C_p (T_{F-ad} - T_s) \right]} + \frac{1}{2} \left[\frac{\tau_o}{\tau} - 1 \right]$$

This gives the burning rate increase, Δr , as a function of the added external flux, I_{ex} ; I_F is the radiation feedback from the flame and I_L is the radiation lost from the flame. The equation is rigorously applicable only for $\Delta r \ll r_o$. It is more general than the equation in Sec. (A) in that no specific assumptions are made concerning the behavior of the gaseous flame except that it can be characterized by a reaction time τ . The above equation is essentially the result of a heat balance on a solid regressing under the influence of its own self-sustained flame, perturbed by an added external flux of radiation. The same comments made in Section (A) regarding the difficulties of both a numerical and experimental nature apply here as well. No experimental work was done along these lines.

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13. ABSTRACT <p>An experimental situation was devised in which the gaseous flame of a regressing solid propellant was suppressed and replaced by a radiative input to the sample surface so as to allow a detailed examination of the energetics of propellant gasification. The desired flameless regression condition was attained for at least two PBAA/AP compositions. However, two seriously detrimental effects entered into the experiments: an abnormally large proportion of AP was ejected from the regressing sample surface and the unejected fraction largely sublimed without further reaction. The combination of these two factors and the very low pressures required in the tests severely limits the applicability of the results to normal propellant combustion.</p> <p>The original objective was to achieve a state of artificial burning driven by radiant energy in which everything that occurs at the surface and in the solid phase would be exactly the same as in normal burning, except that the heat feedback from the normal gas flame would be entirely replaced by an easily measurable heat flux from the radiation source. The comparison would have provided an excellent diagnosis of the energetic processes in normal flame propagation. Although the experiment failed to achieve its original objective for the reasons mentioned, several important things were learned about combustion processes at low pressures.</p>		

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